

Direct Synthesis of Hydrazine Through Nitrogen Fixation
by means of Two-Photon Absorptions

Field of the Invention

The present invention relates to two nitrogen fixation methods using two-photon absorptions that excite N_2 from its vibrational state using nanosecond high-energy laser pulses of wavelengths near infrared and blue-purple ranges. This excited nitrogen is then made to interact to form hydrazine in either high-pressure N_2 - H_2 gas mixtures or with N_2 embedded in water. Hydrazine formation based on this laser induced chemistry produces liquid hydrazine which, of practical interest, can exist at room temperature and atmospheric pressure.

Background of the Invention

A number of experimental and theoretical efforts for producing hydrazine based on direct synthesis of N_2 and H_2 as well as preparation by nitrogen fixation have been undertaken during the past several decades. Most consisted of attempts to stimulate inert H_2 into bonding with N_2 . At best, however, the end product was ammonia. Traces of N_2H_4 were detected in some cases, but the yield was in the fractional per cent range and did not warrant commercial exploitation. Stimulation of the N_2 - H_2 reaction by glow discharge, β -radiation, and α -radiation has also been tried, but no practical results were obtained.

Some experimental efforts were made by Olin et al [J. Chem. Eng. Data, 6, 384 (1991)] under conditions of extreme pressure (667MPa) and temperature (8000 K), such as those achieved for a few milliseconds in a ballistic piston apparatus containing N_2 and H_2 . This method also failed to produce N_2H_4 from its elements. This is due to the fact that N_2 is a very inert molecule, making it very difficult to form any chemical compound directly from N_2 . As will be explained later, the temperatures ($\sim 8000K$) turn out to be not high enough to overcome the activation

energy requirement. Also the confinement time is too short for the reaction to go to completion. Nevertheless, the energy differentials involved in reductive fixation of N_2 have shown that a catalytic process is possible under mildly reducing conditions only. It requires the cooperation of powerful reactants with an absolute potential energy of not less than 1.4 eV. Other than a catalytic approach, however, one based on laser chemistry is also workable as described below.

In order to overcome the difficulties of N_2H_4 formation by means of direct nitrogen fixation, an energy of activation to promote elementary chemical reactions must be considered for practical applications; that is, in order that the reaction may take place, the stored energy of the system must be raised a certain amount above that of the initial state, or in other words, a potential barrier must be overcome in going from the initial to the final states. This barrier can be high for reactions between saturated molecules; however, it can also be high for reactions in which radicals or free atoms take part, as will be demonstrated for $N_2 + 2 H_2 = N_2H_4$ that is considered below.

Activation energies were first treated theoretically as an application of quantum mechanics by London [Z. Elektrochem. 35, 552(1929)]. Based on knowledge of the potential curves of the participating diatomic molecules, it is possible to predict the approximate magnitude of the activation energy. A quantitative determination can then be made using the experimental data of enthalpy of formation. In this connection, one may mention that diazene, $HN=NH$, is a short-lived intermediate of N_2H_4 decomposition and possibly also an intermediary of hydrazine formation through N_2 fixation. It is important to know its heat of formation in order to calculate the heat of reactions involving N_2H_2 as it forms hydrazine. A standard enthalpy of formation for the trans isomer has been measured in a mass spectrometer and calculated from appearance potentials,

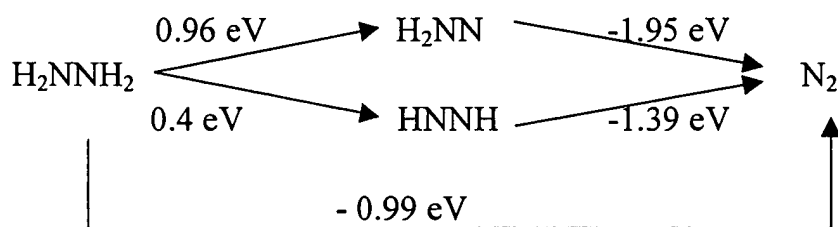
$$(\Delta H)_{298}^f = (212 \pm 8) \text{ KJ/mol}$$

[see Foner et al, J. Chem. Phys. 68, 3162 (1978), *ibid*, P.3169-3171; Frost et al, J. Chem. Phys. 64, 4719 (1976)]. Some of the earlier reported enthalpy data were those of Willis et al [Can. J. Chem. 54, 1 (1976); *ibid*, 47, 3007 (1969)], who prepared N_2H_2 by microwave discharge in a hydrazine vapor. Their data resulted in a heat of formation of diazene, of

$$(\Delta H)_{298}^f = (151 \pm 8) \text{ KJ/mol}$$

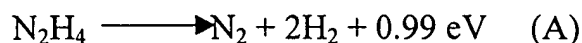
The ionization potential of N_2H_4 in their tests was found to be $(9.7 \pm 0.1) \text{ eV}$, and the ionization potential of the N_2H radical was 7.6 eV.

Another contribution to this question is the work by Wiberg, et al [Z. Naturf. 34B, 1385(1979)] who calculated the heat of formation of trans-diazene from ionization and appearance potentials of the molecule fragment to be 134 KJ/mol. The enthalpy of isomerization to iso-diazene is 54 KJ/mol. The N-N and the N-H dissociation energies are 510 KJ/mol and 339 KJ/mol, respectively. The energetic relationships between N_2H_4 and its dehydrogenation products are shown schematically below



This is the energy scheme of dehydrogenation of hydrazine with hydrogen extracted as H_2 . Diazene is thus in analogy to N_2H_4 , an endothermic compound, and it is expected to decompose spontaneously.

The above considerations then imply



which, in turn, implies that the activation energy for N_2H_4 formation from N_2 and two hydrogen molecules is 0.99 eV. A comparable amount of energy can be stored in N_2 as vibrational energy. In order to have a quantitative description we follow the customary formulation where the energy levels of a diatomic molecule may be written as

$$\left. \begin{aligned} E_{v,J} &= E_{vib} + E_{rot} \\ E_{vib} &= \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \dots \\ E_{rot} &= B_v J(J+1) - D_v[J(J+1)]^2 + \dots \end{aligned} \right\} \quad (1)$$

where

$$\begin{aligned} B_v &= B_e - \alpha_e(v + 1/2) + \dots \\ D_v &= D_e + \dots \end{aligned}$$

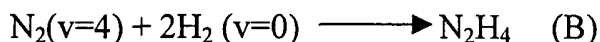
Here v and J are the vibrational and rotational quantum numbers, respectively. In this customary formulation, the constants ω_e , B_e , etc., as tabulated for diatomic molecules, are given in units of cm^{-1} . For N_2 , we have

$$\begin{aligned} \omega_e &= 2358.57 \text{ cm}^{-1} \\ \omega_e x_e &= 14.32 \text{ cm}^{-1} \\ B_e &= 1.99824 \text{ cm}^{-1} \\ \alpha_e &= 0.017318 \text{ cm}^{-1} \\ D_e &= 5.76 \times 10^{-6} \text{ cm}^{-1} \end{aligned}$$

To convert cm^{-1} to eV, one uses $1 \text{ eV} = 8068.3 \text{ cm}^{-1}$. For a vibrational quantum number $v=4$, we have

$$E_{v=4,J=0} - E_{v=0,J=0} = 1.13 \text{ eV} > 0.99 \text{ eV}$$

which is larger than the required activation energy, and one should expect that

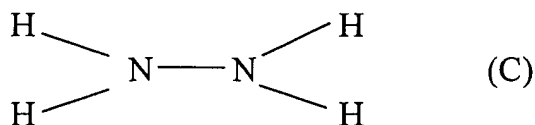


A method of obtaining $N_2(v=4)$ from $N_2(v=0)$ begins when $N_2(v=0)$ is pumped to $N_2(v=8)$ by two-photon absorption with high energy, short pulse Nd: YAG lasers ($\lambda=1.06 \mu m$) providing the photons. As will be shown below, under intense laser irradiation, half of the N_2 will end up in the $v=8$ state, while the other half will

remain in the $v=0$ state when the two-state up and down transitions between $v=0$ and $v=8$ are saturated. If this excited gas of N_2 is subsequently compressed at high pressures ($\sim 100\text{Atm}$), then because of near-resonant V-V energy transfers an energy equilibrium will be reached when all N_2 molecules are in the $v=4$ state, and no further energy exchanges between these molecules are possible. When $N_2(v=4)$ gas mixes with H_2 gas with the molar ratio of 1:2 as in (B) under the conditions of high gas pressure and low temperatures ($\sim 300\text{ K}$), liquid hydrazine will be formed.

One may point out that the physical concept just described is in fact a very common practice in the scientific community. The most prominent example is excimer lasers, such as $XeCl$ and KrF . As is well known, Xe and Kr are inert gases like He, Ne, and Ar; they don't react with other atoms in their ground states. However, when Xe or Kr is pumped to an excited state, it becomes chemically active, and will react with Cl and F to form bound diatomic molecules $XeCl$ and KrF , respectively. Thus the failure to entice N_2 to react with H_2 can be understood to occur because certain energy conditions are required that are not properly met. My proposed methods to satisfy the required energy condition will thus have important practical consequences.

There remains an important scientific issue concerning how reaction (B) takes place. In addition to energy considerations and the relationship that (A) is a reverse process to (B), a number of intermediate chemical processes occur before the final product, which is N_2H_4 , forms as in reaction (B). From the known molecular structure of N_2H_4 , namely,



The intermediate step in reaction (B) must therefore involve an electron transfer process. The experimental evidence as well as the theoretical basis for hydrazine

electron transfer (ET) chemistry have been extensively established by a number of investigators. The following review articles and papers contain the scientific information that underlies and supports the present invention:

- (a) S.F. Nelson, "Molecular Structure and Energetics". In Liebman et al, Eds.; VCH Publishers, Inc., Deerfield Beach, FL., 1986, Vol. 3, Chapter 1;
(b) S.F. Nelson, Acc. Chem. Res. 14, 131 (1981); and
(c) K. Kobuta et al, J. Phys. Chem.. 86, 602 (1982).

Finally, I wish to point out that hydrazine is in many respects very much like water. The following table compares several important physical properties of those two substances. Also included are the boiling points of H₂, N₂ and O₂. They are, of course, very different from those of N₂H₄ and H₂O. It appears that hydrazine is suitable to replace gasoline for internal combustion engine if the price is right.

	H ₂ O	N ₂ H ₄	H ₂	N ₂	O ₂
Molecular Weight, g/mol	18	32	2	28	32
Boiling point, °C	100	113.5	-258	-196	-183
Melting point, °C	0	1.8			
Liquid density, g/cm ³	1	0.997			
Vapor pressure, Torr(mmHg)	25	10.4			
Dielectric constant	78.3	51.7			

Brief Summary of the Invention

The present invention is based on a rigorous investigation of the interaction

process between a homonuclear diatomic molecule and a radiation pulse and then another homonuclear diatomic molecule. As a result of this investigation, I discovered two methods of directly synthesizing hydrazine by means of nitrogen fixation. The first method uses N_2 and H_2 as the raw materials for producing N_2H_4 , while the second method utilizes N_2 and H_2O as the raw materials.

It is well known that N_2 in its ground state is very inert as in air, and chemically inactive much like He, Ne, Ar, Kr, and Xe. However, when N_2 is excited by electron impact or through absorption of radiation, it can readily interact with other molecules just like Kr or Xe in excimer lasers.

For N_2 to interact specifically with two H_2 to form N_2H_4 , one cannot utilize an arbitrary excitation of N_2 . Only a specific excitation can accomplish the desired goal of having good efficiency and practical application of the method. The specific requirement for N_2 is to store only enough energy (in slight excess of the activation energy) for the chemical reaction to take place. The activation energy that is needed for N_2 to react with H_2 to form N_2H_4 is 0.99 eV.

The required 0.99 eV of activation energy can be stored in the $v=4$ vibrational state of N_2 . This energy can be supplied through absorption of radiation. Since N_2 is a homonuclear diatomic molecule which has no permanent electric dipole moment, a single photon absorption with wavelengths in the visible range or longer is forbidden. This explains why the air is transparent to sunlight in the visible range. However, absorption of two photons in N_2 is allowed, producing a transition from the ground vibrational state. This is a common process familiar in nonlinear optics.

A simple calculation can be made to determine the excited vibrational state quantum number v in the ground electronic configuration. However, it should also be pointed out that two-photon absorption processes require high radiation intensity.

Because large numbers of N_2 have to be excited to have any practical interest, the radiation energy should be high and the radiation itself must be a short pulse.

These requirements can be met in the current state of laser technology by high-energy lasers in the near infrared to the visible wavelengths. The laser energy per pulse contemplated here is of the order of 10^5 J/pulse, with a pulse length of one nanosecond or shorter.

Theoretical studies of N_2 and Nd: YAG laser pulse interaction reveal that the excited vibrational state ($v=8$) and the ground vibrational state ($v=0$) become saturated after absorptions of two laser photons ($\lambda=1.06 \mu\text{m}$), i.e., half of the N_2 populate the $v=8$ state, and the remaining half reside in $v=0$. If this $v=0$ and $v=8$ mixture is compressed, then a resonant vibrational-vibrational (V-V) energy transfer process acts over a short time period to redistribute the vibrational quantum states. Quickly, an energy equilibrium is reached when all molecules occupy the $v=4$ state, and no further V-V transfer can occur. In this equilibrium, the $v=4$ state can populate various rotational states with different quantum numbers J . That's where and when energy storage takes place. Further interactions among different J states at $v=4$ are known as rotational-rotational (R-R) transfer. The final distribution in J is determined by Boltzmann's law at the temperature T of the N_2 gas.

The above considerations constitute a two-step technique for generating an N_2 gas composed entirely of nitrogen molecules at this $v=4$ state with the aid of a high-energy short-pulse Nd: YAG laser in the near infrared. The stored energy of N_2 at $v=4$ is about 1.13eV. This energy is larger than the activation energy (0.99eV) for N_2H_4 formation based on direct synthesis of N_2H_4 by nitrogen fixation with H_2 . The subsequent interaction of the excited N_2 vibrational state ($v=4$) with two hydrogen molecules takes place rapidly through an electron transfer (ET) mechanism that is followed by a dissociative recombination process under high

pressure and low-temperature gas conditions. For simplicity, this method is hereinafter referred to as the “dry” hydrazine process.

In another method of N_2 fixation, a gas of excited N_2 is made to interact with H_2O . For simplicity, this method is hereinafter referred to as the “wet” process. An analysis similar to the one just described can likewise be carried out. This method is based on the observation that the combustion of N_2H_4 , i.e., $N_2H_4 + O_2$, produces $N_2 + 2H_2O + 6.02$ eV. The reverse of this process occurs when N_2 is made to store the energy of 6.02 eV. A two-photon absorption from a 0.4 μm laser (the shortest visible blue) will pump the N_2 ground vibrational state to $v=25$ in the ground electronic configuration. This highly excited N_2 is energetic enough to cause the dissociation of $2H_2O$ into $2H_2 + O_2$ while ending up in the $v=4$ state. In this state it can then proceed to react with H_2 to form N_2H_4 as in the first dry method of direct synthesis. The ways and means of H_2O dissociation by N_2 in the $v=25$ state are the reverse of the hydrogen combustion processes and are well known by chemists. In order to get the highest possible H_2O molecule density, one must interact liquid water ($\sim 10^{22}/cm^3$) with an N_2 gas that is pumped into the $v=25$ vibrational state.

It is essential that in the “wet” case of N_2 fixation with H_2O , the N_2 should be maintained throughout the processes at ordinary pressures. At high pressures exceeding several atm, e.g., loss of N_2 at $v=25$ occurs due to V-V transfer, where some of N_2 will end up with $v<25$. Such collisional energy transfers will deplete N_2 molecules of the energy needed to dissociate H_2O . It is tempting to avoid this type of energy redistribution by raising the photon energy. But this encounters two problems: first, the laser will have shorter wavelength where both optics and laser itself are more difficult to come by, and second, high-energy two-photon absorptions lead to N_2 dissociation (the dissociation energy is 7.37 eV). If a single photon absorption is used, the photon energy is about 8.59 eV, putting the N_2 in the

first excited electronic configuration. This state has a very short radiative lifetime ($\sim 10^{-6}$ sec or shorter) due to spontaneous emission of a single photon. In contrast, the radiative lifetime of excited vibrational states that are in the ground electronic configuration is very long ($\sim 10^3$ sec or more). These decays result from
5 spontaneous emission of two photons. Thus in the present "wet" invention there is no loss of excitation through radiative emissions.

Hydrazine can also be made by procedurally reversing the "dry" process previously described with gaseous hydrogen as the source thereof. Hydrogen molecules in a hydrogen pressure tank are attacked by short-pulse laser photons
10 which have been emitted by a high-energy laser generator and then laser energy is greatly increased through a laser amplifier with an energy of 10^6 Joules per pulse, whereby the hydrogen molecules, existing in the ground vibrational state, absorb two high-energy laser photons with 10^{10} Watts/cm² of pulse intensity and can easily surmount the vibrational energy barrier to become hydrogen molecules in the
15 excited vibrational state. When nitrogen molecules are admixed with the excited hydrogen molecules, hydrazine, N₂H₄, is readily produced.

Brief Description of the Drawings

These and other features of the present invention are more fully set forth below in the accompanying detailed description, presented solely for purposes of
20 exemplification and not by way of limitation. In the accompanying drawings, of which:

Fig. 1 is an energy level and transition diagram useful in explaining the present invention,

Fig. 2 is a diagram, generally called a Feynman diagram, illustrating (a) a
25 two-photon absorption process and (b) a two-photon emission process, with typical vibrational states of N₂ indicated.

Fig. 3 is also a Feynman diagram involving two N_2 molecular interactions in the lowest ladder approximation. It illustrates the resonant V-V energy transfer useful in explaining the N_2 -fixation with H_2 .

Fig. 4 is a diagram of the apparatus and processes involved in the dry method 1 of the present invention based on N_2 fixation with H_2 .

Fig. 5 is a diagram of the apparatus and processes involved in the wet method 2 of the present invention based on N_2 fixation with H_2O .

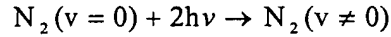
Detailed Description of the Invention

The present invention contemplates a system of photoexcitation and chemical reaction in which an enhanced polyatomic molecule formation efficiency is achieved, that is, more molecules are formed with a minimum of energy input. In particular, photoexcitation occurs through absorption of two photons by an N_2 molecule. Following this photoexcitation, polyatomic molecules are formed in accordance with the method of excited-state laser chemistry. The process thus described is illustrated in Fig. 1 showing first and second energy steps, 12 and 14, starting from a ground state, 16, and proceeding to an intermediate excited state, 18, and ultimately ending in a highly excited state, 20. The intermediate state, 18, belongs to the first excited electronic configuration. The transition through this state is nonresonant. Additionally it is desired and deemed preferable to also excite molecules from other low-lying energy states, such as the different rotational states with quantum number J belonging to the ground vibrational state with quantum number $v=0$ in the ground electronic configuration. All two-photon transitions connecting different rotational states are energetically close to each other due to the selection rules for rotational transitions $\Delta J=0, \pm 1, \pm 2$ in two-photon absorptions and the smallness of the rotational constant for N_2 .

Intense laser radiation is employed here to produce the transitions 12 and 14. It

illuminates a gas of N_2 molecules at approximately one atm pressure, and the laser intensity is chosen to efficiently excite N_2 molecules to a highly excited vibrational state belonging to the ground electronic configuration through absorptions of two laser photons. The photon energy can be determined once the molecules needed to interact with N_2 ($v \neq 0$) are known.

In the above description, I considered only the two-photon absorption process by N_2 . This is the lowest energy possible for radiation absorption by N_2 at visible wavelengths or longer. A single-photon absorption is forbidden since N_2 is a homonuclear molecule having no permanent electric dipole moment. Only the above wavelengths are required since the photon energy must not exceed 3.5 eV. For photon energy larger than 3.5 eV, the efficiency for hydrazine production is degraded because of excessive heat production. The two-photon absorption process depicted in Fig. 1 is



where $N_2(v=0)$ is the initial ground vibrational state denoted as 16 in Fig. 1, $N_2(v \neq 0)$ is the final vibrational state denoted by 20 in Fig. 1, and $h\nu$ is the single-photon energy from a high-energy pulsed laser. The probability of transitioning from the initial state to the final state at the end of the pulse time τ is

$$P_{i \rightarrow f} = \frac{4\xi^2}{\Delta\nu^2 + 4\xi^2} \sin^2\left(\frac{\tau}{2} \sqrt{\Delta\nu^2 + 4\xi^2}\right) \quad (2)$$

where

$$\begin{aligned} \Delta\nu &= E_v - E_0 - 2h\nu \\ \xi &= \pi\alpha_g I \end{aligned} \quad (3)$$

α_g is the ground electronic state polarizability, I is the laser intensity, and ν is the laser frequency. For N_2 ,

$$\alpha_g = 1.7 \times 10^{-24} \text{ cm}^3$$

In practical applications as will be made clear later, the laser intensity must be large enough to have

$$2\xi \gg |\Delta\nu| \quad (4)$$

and

$$\xi\tau \gg 1 \quad (5)$$

Expression (5) may be rewritten as

$$\pi\alpha_g \tilde{E}_L \gg 1 \quad (6)$$

Expression (4) is the condition for a near-resonant absorption where the power broadening parameter 2ξ is much larger than the energy offset (frequency detuning), and

$$\tilde{E}_L = I\tau \quad (7)$$

is the laser pulse energy fluence. Let ϵ_L be the laser energy per pulse and A be the cross sectional area of the laser beam, then

$$\left. \begin{aligned} \tilde{E}_L &= \epsilon_L / A \\ I &= \epsilon_L / (A\tau) \end{aligned} \right\} \quad (8)$$

Under the conditions defined by expressions (4) and (5), the transition probability is

$$\langle P_{i \rightarrow f} \rangle = \frac{1}{2}$$

on average. This means that half of N_2 molecules is in the excited vibrational state v and the remaining half is in the ground vibration state $v=0$.

As an example, consider one mole of N_2 interacting with a high energy Nd: YAG laser for which $\lambda = 1.06 \mu\text{m}$ and $h\nu = 1.12 \text{ eV}$. One mole of N_2 consists of N_A molecules having a total mass of 28 grams, where

$$N_A = 6.02 \times 10^{23}$$

is Avogadro's number. The total number of absorbed photon must be N_A ; thus the

laser energy per pulse must be

$$\varepsilon_L > N_A h \nu = 6.7 \times 10^{23} \text{ eV} \cong 10^5 \text{ J} \quad (9)$$

Let $A=10^3 \text{ cm}^2$, $\tau = 10^{-9} \text{ sec}$, then

$$\tilde{E}_L > 100 \text{ J/cm}^2$$

$$I > 10^{11} \text{ W/cm}^2$$

It is convenient to work in units such that $\hbar/2\pi = c=1$, then

$$1 \text{ W/cm}^2 = 10^{13} \text{ cm}^{-4}$$

$$1 \text{ J/cm}^2 = 3 \times 10^{23} \text{ cm}^{-3}$$

Using the laser intensity 10^{11} W/cm^2 we get for N_2 , the power broadening 2ξ in Eq.

(13),

$$2\xi = 12 \text{ cm}^{-1}$$

For a given laser frequency ν , $\Delta \nu$ is slightly different for transitions involving different rotational quantum numbers J . If (4) is not satisfied for most J of interest, one may increase laser intensity I for a given pulse energy, \tilde{E}_L , by decreasing the pulse length τ through the well known pulse compression technique. For example, if τ is compressed or shortened from 1 ns to 0.1 ns, then $2\xi=120 \text{ cm}^{-1}$; (4) will be satisfied for all J , since the rotational constant B_e for N_2 is small ($B_e=1.99 \text{ cm}^{-1}$).

Note that (5) does not depend on the pulse length τ . For $\tilde{E}_L = 100 \text{ J/cm}^2$, we have

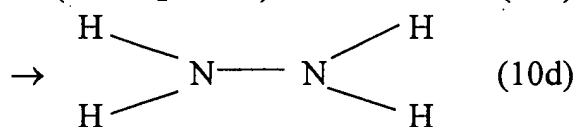
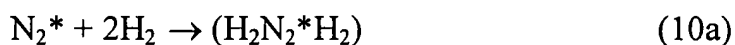
$$\pi\alpha_g \tilde{E}_L = 56\pi \gg 1$$

Therefore, (6) remains satisfied.

The two-photon absorption calculations considered so far are good approximations when the gas pressure is low and a collision-induced single-photon absorption process by a single molecule may be ignored. Two-photon resonant

state transitions at best produce a 50% excited vibrational state population when the pulse intensity is sufficiently high. This is achievable for subnanosecond pulses and ultimately is exploitable for commercial and industrial applications. One anticipates that such a partially excited molecular system can be made to quickly reach a new equilibrated vibrational level under sufficiently high pressure (~100 atm) in which state no further V-V energy transfer can occur. In the above example using Nd: YAG laser (1.06 μm), the final vibrational quantum number reached is $v=4$. The corresponding state into which two photons are absorbed is $v=8$ as mentioned earlier.

Let us denote the type of excited N_2 by N_2^* when almost all N_2 molecules reside in the excited vibrational state $v=4$ as a result of vibrational energy redistribution. The interaction of N_2^* with H_2 gas to produce N_2H_4 is then accomplished by means of dissociative recombination aided by an electron transfer mechanism in the following manner,



Here $(\text{H}_2\text{N}_2^*\text{H}_2)$ in (10a) is a molecular complex, which, due to the van der Waals force, is followed by electron transfer from N_2^* to H_2 as in (10b), an intramolecular relaxation, and a subsequent relaxation from dissociative recombination. This is shown as a two-step transition from (10b) to (10c), a dissociation of H_2^- , and from (10c) to (10d), final recombination to form N_2H_4 . All this chemistry can be effective since N_2^* stores an amount of energy that is greater than the activation energy (0.99 eV), and can be made to take place efficiently if the pressure (~100 atm) is sufficiently high, and the temperature (~300°K) is kept low enough by heat

transfer, such as by cooling with water. This is due to the facts that the formation of molecular complexes is strongly pressure dependent, since it requires a three-body interaction, and that the time for interaction must be long enough, which can be attained only at relative low temperatures.

It is perhaps useful to explain how the transition probability given in Eq. (2) is obtained. The elementary processes responsible for a transition of this kind are depicted in Figs. 2(a) and 2(b). In Figs. 2(a) and 2(b), the solid lines with arrows represent an N_2 molecule, and an arrowed wavy line represents a photon being absorbed (toward the solid line) or emitted (away from the solid line). Fig. 2(a) illustrates absorption of two photons, 22 and 24, by N_2 which is in ground vibrational state $v=0$ designated as 15. In the first photon absorption, 22, N_2 transitions to the nonresonant intermediate state 19 (belonging to the first excited electronic configuration). In the second photon absorption, 24, N_2 moves into the vibrational state, 17, with $v=0$. Both states, 15 and 17, for N_2 are ground electronic configurations. Fig. 2(b) is the reverse process of Fig. 2(a) wherein absorptions in Fig. 2(a) become emissions in Fig. 2(b). The description of Fig. 2(b) parallels that of Fig. 2(a) in a straightforward manner (emission replacing absorption) and will not be repeated here, except to note that 21 is the same as 19, both belonging to the first excited electronic configuration of N_2 . Furthermore, it should be noted that Fig. 2(a) describes a process that cannot take place in the absence of external radiation, but the Fig. 2(b) process can take place even when no external radiation is present.

It is important to know how long the N_2 molecules will stay in the excited vibrational state after a two-photon absorption. The lifetime needs to be sufficiently long to have practical interest. When the gas pressure is sufficiently low, the fundamental loss mechanism of N_2 excited vibrational states is through the

spontaneous emission of two photons. The Feynman diagram corresponding to this situation is given in Fig. 2(b). The two photons, 26 and 28, can be different.

The first photon 26 is labeled by $(\vec{\kappa}_1, \hat{e}_1)$, and the second photon 28 is labeled by

$(\vec{\kappa}_2, \hat{e}_2)$, where $\vec{\kappa}_1$ and \hat{e}_1 denote the photon wave vector and unit polarization

vector, respectively. For completeness, one briefly summarizes the calculation of the spontaneous two-photon emission rate and the associated lifetime of an excited vibrational state in the ground electronic configuration as follows.

Using the Feynman rules, one finds that the transition amplitude for spontaneously emitting two photons from the excited vibrational state $|i\rangle$ to the ground vibrational state $|f\rangle$ corresponding to Fig. 2(b), is given by

$$A_{fi}(\vec{\kappa}_1, \hat{e}_1; \vec{\kappa}_2, \hat{e}_2) = \frac{2\pi e^2}{\sqrt{2k_1 V} \sqrt{2k_2 V}} M_{fi} \delta(E_i - E_f - k_1 - k_2)$$

where

$$M_{fi} = \frac{1}{m^2} \sum_n \frac{\langle i | \vec{p} \cdot \hat{e}_1 e^{i\vec{k}_1 \cdot \vec{r}} | n \rangle \langle n | \vec{p} \cdot \hat{e}_2 e^{i\vec{k}_2 \cdot \vec{r}} | f \rangle}{E_i - E_n - k_1} + (\vec{k}_1 \hat{e}_1 \leftrightarrow \vec{k}_2 \hat{e}_2, k_1 \leftrightarrow k_2)$$

The two-photon spontaneous emission rate γ_v is

$$\gamma_v = \sum_{\hat{e}_1} \sum_{\hat{e}_2} V \int \frac{d^3 k_1}{(2\pi)^3} V \int \frac{d^3 k_2}{(2\pi)^3} |A_{fi}(\vec{k}_1, \hat{e}_1; \vec{k}_2, \hat{e}_2)|^2$$

With the usual substitution,

$$[2\pi\delta(E_i - E_f - k_1 - k_2)]^2 = 2\pi\delta(E_i - E_f - k_1 - k_2)$$

and the fact that E_n is the energy of the first excited electronic configuration or higher, which implies

$$E_n - E_i \gg k_1 \text{ or } k_2$$

one may approximate the matrix element M_{fi} as

$$M_{fi} = 2 \sum_n \frac{\langle i | \hat{k}_1 \cdot \vec{r} | n \rangle \langle n | \vec{k}_2 \cdot \vec{r} | f \rangle}{E_i - E_n}$$

where the dipole approximation has been made. Let the ground electronic polarizability be α_g , where

$$\alpha_g = \frac{e^2}{4\pi} \sum_n \frac{\langle i | z | n \rangle \langle n | z | f \rangle}{E_n - E_i}$$

5 and for N_2 , $\alpha_g = 1.7 \times 10^{-24} \text{ cm}^3$ as before.

Carrying out the \vec{k}_1 and \vec{k}_2 integrations, we have finally the expression

$$\gamma_v = \frac{8\omega_v^7}{315\pi} |\alpha_g|^2 \quad (11)$$

where

$$\omega_v = E_f - E_i = E_v - E_o$$

10 In the case of N_2 fixation with H_2 as catalyzed by two-photon absorption of Nd:YAG laser radiation, one has that

$$\begin{aligned} \lambda &= 1.06 \mu m \\ \nu &= 9432 \text{ cm}^{-1} \end{aligned}$$

and

$$\omega_v = 2(2\pi\nu)$$

15 corresponds to $v = 8$. The lifetime τ_v for $v=8$ quantum state against spontaneous emissions of two photons is thus found from (11) to be

$$\tau_v = \gamma_v^{-1} = 15 \text{ days}$$

Therefore, at ordinary gas pressures, there is no excitation loss resulting from emissions of two photons. This two-photon lifetime is very long in contrast to the much shorter single-photon spontaneous emission lifetimes which are typically of the order of 10^{-6} to 10^{-9} seconds. It is also seen to be much longer compared to the process time envisioned here for N_2H_4 production, or to other de-excitation

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processes due to collisions of various kinds when the gas pressure is high, e.g. ~ 100 atm. We will address the issue of collision rates below.

High N_2 gas pressure is needed for N_2 fixation with H_2 because the V-V transfer that produces the $v=4$ vibrational energy distribution has improved efficiency as the pressure increases. It is therefore appropriate to briefly describe the physics involved. The best way to illustrate the interaction is to employ the Feynman diagrams shown in Fig. 3, commonly referred to as ladder diagrams. In contrast to Fig. 2, the unarrowed wavy lines refer to virtual photons. The interaction of two ground electronic state molecules of homonuclear type must at least involve the exchange of two virtual photons, 35 and 45. The other directed solid lines have the same interpretation as in Fig. 2. Thus the internal solid lines 36, 37, 46, and 47 refer to N_2 in its first excited electronic configuration or higher. The remaining portions of the drawing, namely, 31, 33, 32, 34, 41, 43, 42, and 44, have the same meaning as 15, 17, 11, and 13 in Fig. 2.

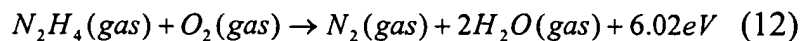
The calculation of the V-V energy transfer rates is carried out in similar fashion to the calculation of the spontaneous two-photon emission rate γ_v considered earlier, except that the algebra is lengthy and tedious. The actual evaluation requires computer work involving numerical integrations of multiple integrals. One will not reproduce the detail here and only state that at ordinary gas pressure and temperature, the V-V transfer rate is about 0.03 sec^{-1} . Thus the collisional energy transfer limited lifetime is of the order of 30 sec. In order to shorten the process time of N_2 fixation with H_2 , therefore, the N_2 gas should be compressed to a pressure of 100 atm or more. At this pressure, the vibrational population redistribution time is only about one second or less.

The process for producing $N_2 H_4$ using N_2 and H_2 as raw materials will now be described. This process is shown in Fig. 4. The N_2 source 50 may come from the

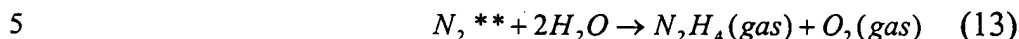
evaporation of liquid nitrogen. Flow duct 51 that directs the N₂ – laser interaction chamber 53, which is equipped with an optical window 72 having a cross-sectional area equal to the laser beam size. A high-energy laser pulse generator 58 emits photons 57 that enter the laser amplifier 56, which is being pumped by an arc lamp 61 that emits light 73 in the desirable spectral range. The arc lamp radiation is absorbed and stored in the laser amplifier 56. The working medium in 56 may be either a gas or liquid dye of suitable kind for the desired spectral range. On passing through the laser amplifier, the outgoing laser photons 55 acquire the needed intensity and enter the window 72 to interact with the N₂ molecules in 53 where each N₂ absorbs two laser photons. After interaction, any unabsorbed photons 52 then leave the interaction chamber 53. The N₂ gas, after laser pulse interaction in 53, then flows through duct 54 and enters the high-pressure gas chamber 59 operated at 100 atm or more. Gas chamber 59 is equipped with a piston to handle high-pressure gas operations. After compression, the gas leaves 59 through duct 60 and is introduced into vessel 62 where hydrogen flows from source 63 through duct 64. The N₂ and H₂ interaction chamber 62 is surrounded by a cooling system 70. Water flows through duct 65 passing through 69 and 67, and leaves through duct 66. This water cooling system also includes a heat exchanger (not shown). The final hydrazine product is collected at container 71 through duct 68.

One now moves on to consider in the present invention a second method of “wet” hydrazine synthesis using N₂ and H₂O as raw materials. It is well known that hydrazine can be used as a rocket propellant and as a corrosion inhibitor for steel structures that are in contact with hot water. These uses stem from the facts that hydrazine is an endothermic compound ($\Delta_f H^\circ_{298} = 95.4 \text{ KJ/mole}$), and that the

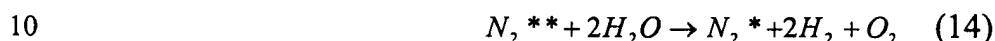
following reaction,



is exothermic by 580 KJ/mol or 6.02 eV/molecule. Reaction (12) then suggests a reverse reaction of the form,

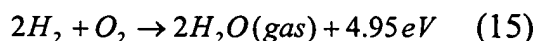


if the vibrational energy stored in N_2^{**} is greater than 6.02 eV/molecule. It is clear, from the earlier discussion concerning hydrazine formation using N_2 and H_2 as raw materials, that the intermediate chemical reaction in (13) must involve the dissociation of H_2O by N_2^{**} , namely,



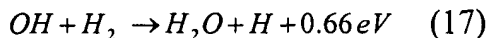
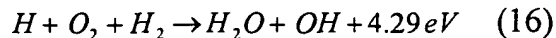
It now follows from (10) that N_2^* has a stored vibrational energy greater than the 0.99 eV activation energy for hydrazine formation, since this reaction completes the process of forming hydrazine from H_2O .

15 In order to determine the vibrational states associated with N_2^{**} and N_2^* , and also to elucidate the mechanism of H_2O dissociation by N_2^{**} in (14), it is useful to begin with the combustion of H_2 described by



Reaction (14) is closely related to the reverse reaction (15). A careful analysis of the H_2 combustion will thus help one understand (14).

20 It is known that (15) does not occur simply by the collision of two hydrogen molecules with an oxygen molecule. Indeed the observation of OH bands in an oxy-hydrogen flame (known as chemiluminescence) shows that OH radicals play an important part in the reaction. One is led to postulate that the following two-step elementary reactions go into the formation of H_2O .



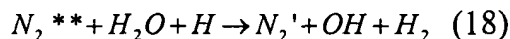
This means that H atoms need to be formed (e.g., by ignition), and that each H atom produces an OH radical and an H₂O molecule according to (16). Each OH radical, in turn, forms an H₂ molecule and regenerates an H atom according to (17).

Process (16) can begin again and we see that H atoms are needed to catalyze the formation of H₂O from the combustion of H₂.

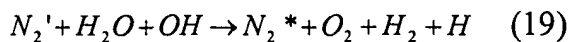
Now in the case of reaction (14), we use the v=25 state of N₂** to catalyze the reverse reaction. This stores the required energy to allow the present invention to work. The N₂** is found to have energy of 6.15 eV above the ground state. The dissociation of H₂O into H and OH takes 5.14 eV. This means that N₂** will lose 5.14 eV of its vibrational energy in catalyzing the reaction. Thus it will make transition from v=25 to a v=3 state that has associated with it some rotational quantum number J, such that

$$E_{3,J} = 1.16 eV$$

according to the energy conservation requirement. If we now assume that H atoms are needed within our system to initiate a chain reaction of the kind similar to the H₂ combustion above, then similar to (17), we have



where N₂' is in the vibrational state with v=22. Likewise, from the reverse reaction (16),



where N₂* is in the vibrational state with v=4.

It should be pointed out that in (18) and (19), because of the requirement of energy conservation, in addition to the vibrational quantum number v , a rotational quantum number J must also be determined. Using $E_{v,J}$, the molecular energy level, the same as Eqs. (1), then for (18) and (19) to go, we must have

$$\begin{aligned} E_{25,J} - E_{22,J'} &= 0.62 + \Delta E_{J,J'}^{(1)} \\ E_{22,J'} - E_{4,J''} &= 4.4 + \Delta E_{J',J''}^{(2)} \end{aligned} \quad (20)$$

With the aid of Eq. (1), one can then find the required J , J' and J'' values that satisfy

$$\begin{aligned} \Delta E_{J,J'}^{(1)} &= 0.04 \text{ eV} \\ \Delta E_{J',J''}^{(2)} &= -0.11 \text{ eV} \end{aligned}$$

Thus a catalytic chain reaction for (14) exists in analogy to (15). Adding (18) and (19), we obtain (14) with N_2^* having the vibrational-rotational energy of 1.13 eV relative to the ground vibrational-rotational state. Subsequently one obtains Eq. (10) since the energy available from N_2^* is greater than the hydrazine activation energy of 0.99 eV.

The theoretical description just made implies that we must use the shortest visible high-power blue laser, which has a wavelength near 4000Å, with corresponding single-photon energy

$$h\nu = 3.1 \text{ eV}$$

The two-photon absorption required will then pump the N_2 , $v=0$ state into $v=25$, which has energy 6.10 eV above the $v=0$ state. The two-photon spontaneous radiative lifetime of the $v=25$ state can likewise be computed. One finds from (11) that

$$\tau_{25} \cong 2200 \text{ sec} \cong 37 \text{ min.}$$

One thus expects no excitation loss to the spontaneous radiative emission process. However, it is important to estimate loss due to possible collisional deactivations,

the most important one being V-V transfer. This is again caused by the saturated nature of the two-photon absorption process between $v=0$ and $v=25$ states, when a pulse laser intensity of $\sim 10^{11}$ W/cm² is used. The V-V transfer rate on the basis of the process depicted in Fig. 3 is found to be of the order of 0.01 sec⁻¹ at an N₂ density of $\sim 10^{19}$ cm⁻³. The de-excitation time is then about 100 sec, which is considerably longer than the processing time for N₂H₄ production that is envisaged here. However, were N₂ to be raised in pressure by two orders of magnitude as in the first method of hydrazine production, the N₂** loss would not be negligible. Thus in the actual practice of the art for N₂ fixation with water, the N₂ density must be kept at 10^{19} cm⁻³ or lower.

The laser energy requirement at $\lambda = 4000\text{\AA}$ may likewise be computed for the production of a given quantity of N₂H₄. The result is similar to the one for N₂ fixation with H₂.

Now that the process and parameters for practicing N₂ fixation with water have been described, the structure useful for practicing it needs to be described. With reference to Fig. 5, a high-energy pulsed-laser source 80 is shown with photons 82 entering laser amplifier 81 which in turn is pumped by flashlamp 85 generating radiation with the desired spectral range that enters amplifier 81 through optical system 84. Photons 83 after laser amplification then go through window 72 of equal area as in Fig. 4. The window material in the present method is different from the first method shown in Fig. 4. The window material for the first method in Fig. 4 must be made suitable for red to far infrared radiation transmission, while for Fig. 5 it must be transparent to blue-purple light.

The photons 83 then interact with N₂, which originates from a nitrogen source 86 that goes through duct 87 and enters into the N₂ – laser interaction chamber 89. Any leftover outgoing photons after interaction are indicated as 88. The gas then

leaves through duct 90. It consists of half of the molecules in the excited vibrational state and the remaining half in the normal ground state. It flows into a vessel 94. Pure water from input 91 flowing through pipe 92 also enters into 94. The water cooling system 95 with water from 97 and recirculating system 96 is the same as in Fig. 4. After the $\text{N}_2\text{-H}_2\text{O}$ mixture interacts in the vessel 94, N_2H_4 liquid is formed. The liquids consisting of N_2H_4 and water then fall through the air duct 101 into vessel 99 in which liquid N_2H_4 and water remain in the bottom of the tank 100, while N_2 and O_2 bubble out through valve 98.

The above-described method and apparatus is intended to be exemplary only of the invention which is to be limited only in accordance with the following claims.